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(71) Applicant: **USS ENGINEERS AND CONSULTANTS, INC.**
600 Grant Street
Pittsburgh Pennsylvania 15230(US)

(72) Inventor: **DiNardo, Victor Martin**
103 Garofolo Drive
Monroeville Pennsylvania 15146(US)

(74) Representative: **Patentanwälte Grünecker, Dr. Kinkeldey, Dr. Stockmair, Dr. Schumann, Jakob, Dr. Bezold, Meister, Hilgers, Dr. Meyer-Plath**
Maximilianstrasse 58
D-8000 München 22(DE)

(54) **Modified polypropylene for film.**

(57) An improved polypropylene blend for biaxial orientation into thin films is made by combining low melt-flow polypropylene, a nucleating agent, and linear low density polyethylene in a pelletizing extruder. Preferably, the low melt-flow polypropylene is formed by cracking a lower melt flow polypropylene with a peroxide agent.

Croydon Printing Company Ltd

SPECIFICATION

VICTOR M. DINARDO

MODIFIED POLYPROPYLENE FOR FILM

BACKGROUND OF THE INVENTION

This invention relates to polypropylene, particularly to polypropylene modified to produce biaxially oriented film for the packaging market. Biaxial orientation is well known in the industry and is used to enhance both the optical and physical properties of the polymer film. Contemporary commercial technology for specialty films involves composite structures that can contain as many as 5 to 7 different coextruded polymeric components. Coextrusion with polymers other than polypropylene is used to improve or impart special properties to the polypropylene such as impermeability or sealability.

To maintain compatibility and clarity of the composite, polypropylene must be used which is known to have a low haze property. Historically, high clarity polypropylene is obtained by modifying the polymer microstructure; the addition of a suitable nucleating agent (i.e. sodium benzoate) to the polymer during pelletizing is known to alter crystalline structure (spherulite growth) and enhance clarity. This improved clarity, however, can be at the expense of good processability and non-uniform properties in the film. For example, optical or mechanical defects such as tearing of the film during drawing can be caused by inhomogeneities (i.e. large particle size distributions) related to the presence of nucleating agents or other inorganic additives.

The present invention provides for the production of a film grade polypropylene that is nucleated, easy to process, has exceptional multi-directional physical properties, and exhibits a low measure of haze. Such a combination of properties has been extremely difficult to achieve in the past.

Prior to the present invention, it has been known that bis(alkylbenzylidene) sorbitols could be used as clarifying agents, i.e. to reduce haze, in polyolefins. See the sales sheet for "Millad 3905";

also see abstracts of the Japanese Patents Appln. 81/186,663, November 19, 1981; Appln. 81/166,675, October 19, 1981, and U. S. Patent Appln. 363,824, March 31, 1982.

It is also known in the art that so-called "controlled rheology" (CR) in polypropylene can be attained by the closely regulated addition of certain peroxides such as 2,5-dimethyl-2,5 di(t-butylperoxy) hexane. The peroxide typically is added in the extruder during pelletization (after the polymerization process is complete). The peroxide will tend to encourage a more or less uniform breakdown of the molecular structure of the polypropylene under the physical and thermal stress of the extruder, resulting in a product having a relatively narrow molecular weight distribution; the reduction in average molecular weight and the improved narrowness of the molecular weight distribution are typically accompanied by an increase in melt flow and a change in both rheology and physical properties compared to those of a reactor product have a similar melt flow. This "cracking" technique is well known in melt spinning fibres and more recently has become accepted in high-speed injection molding; however, film made from low melt flow peroxide-cracked material is "flexible" and has a high percent haze, two undesirable properties for polypropylene films.

It has also been suggested in the prior art that so-called linear low density polyethylene may be used to make films. Linear low density polyethylene (LLDPE) is polyethylene containing a small amount (typically 0.5%) mono olefin co-monomer such as 1-hexene, 1-butene, or 1-octene and generally having a relatively narrow molecular weight distribution and short chain branching. See, for example, U.S. Patent 4,362,835. It is indicated in German Patent 1,902,573 that the incorporation of polyethylene (homopolymer) may have an effect on the crystallization rates of polypropylene.

A physical mixture of a propylene/ethyl random copolymer and a small amount of linear low density polyethylene which may contain as a "third component", among other possibilities, dibenzylidene sorbitol is described in U.S. Patent 4,434,264. The blend is said to be useful for impact strength; no benefits are described in the areas of film-making, or biaxial orientation.

The reader may be interested also in U.S. Patents 4,359,544; 4,282,076 and 4,296,022 for general background in the area of nucleation and controlled rheology.

It is an object of the present invention to provide a film grade polypropylene composition that is nucleated, easy to process and has improved biaxial properties.

In accordance with the present invention a polypropylene composition is provided comprising:

(a) a propylene polymer having a melt flow of about 2.0 to about 5.0 g/10 min.(L),

(b) about 0.10 wt % to about 0.25 wt % dibenzylidene sorbitol nucleating agent and

(c) a linear low density ethylene copolymer comprising ethylene copolymerised with olefin monomers having about 4 to about 8 carbon atoms,
characterised in that
said propylene polymer (a) is a propylene homopolymer; said bibenzylidene sorbitol nucleating agent (b) is a bis(alkylbenzylidene) sorbitol wherein the alkyl groups have about 2 to 18 carbon atoms; and said linear low density ethylene copolymer (c) comprises ethylene copolymerized with about 0.5 to about 7% of said olefin monomers, has a melting point of about 120°C and is present in an amount of about 0.25 wt % to about 2.0 wt %.

Besides the benefits of improved processability in the area of film-making, the polypropylene composition of the invention has exceptional multi-directional physical properties, and exhibits a low measure of haze. Such a combination of properties has been extremely difficult to achieve in the past.

In a preferred embodiment, the propylene homopolymer is formed by cracking a lower melt flow polypropylene using a peroxide agent selected from the group consisting of dialkyl peroxides in an amount of about 50 ppm to about 300 ppm. The low melt flow propylene homopolymer may be created , for example, in an extruder from a lower melt flow propylene homopolymer by adding thereto prior to or during the extrusion process about 100 ppm to about 250 ppm of a dialkyl peroxide "controlled rheology" additive such as Lupersol 101.
The use of a peroxide cracked propylene homopolymer is, in particular, useful to effect an increase in the polypropylene crystallisation temperature to coincide approximately with the melting point of the linear low density ethylene copolymer. This thermal balance, and the concurrent crystallisation of ethylene copolymer and polypropylene may effectively contribute to low haze and improved physical properties.

The propylene homopolymer, after cracking, has preferably a molecular weight distribution of about 2 to about 4 and a crystallisation temperature of about 120°C.

The composition of the present invention may include about 750 to about 1500 ppm of more or less conventional stabilizers, such as BHT, calcium stearate, Irganox 1010, and Kenemide E. The substituted sorbitol nucleating agent as contained in the composition of the present invention in an amount of about 1000 ppm to about 2500 ppm is a bis(alkylbenzylidene) sorbitol wherein the alkyl groups have about 2 to about 18 carbon atoms (specifically Millad 3905). The linear low density ethylene copolymer as contained in the composition of the invention is typically, a polyethylene including about 0.5 % to about 1.0 % mono olefin monomers having from 4 to 8 carbon atoms and having a melt flow of about 1.0 to about 2.5 (condition E).

The polypropylene compositions of the present invention are, in particular, useful for producing biaxially oriented films or sheets. Accordingly, the present invention provides a polypropylene composition useful for producing film, produced by a process comprising, for example, cracking a polypropylene having a melt flow lower than 5.0 g/10 min.(L) with a dialkyl peroxide in the presence of about 0.10 wt. % to about 0.25 wt. % sorbitol nucleating agent and about 0.25 wt. % to about 2.0 wt. % linear low density polyethylene comprising ethylene copolymerized with about 0.5 % to about 7 % olefin monomers having about 4 to about 8 carbon atoms, to effect an increase in the polypropylene crystallisation temperature to coincide approximately with the melting point of the polyethylene. Preferably, the crystallisation temperature of the polypropylene and the melting point of the linear low density polyethylene are both about 120°C.

Several analytical comparisons (Table I) have been made which illustrate the advantages of this invention. In Table I, PP-A is a fractional melt flow (0.70, condition L) reactor-made homopolymer. This material is the "base" or "starter" resin which, as used in columns II, III and IV of Table I is peroxide cracked to the final product.

Table I

Analytical Results - Nucleated CR Polypropylene Containing LLDPE

	I	II	III	IV	V
	PP-A	PP-A + 120 ppm Peroxide	PP-A + 120 ppm Peroxide + Additives*	PP-A + 120 ppm Peroxide + Additive + 1.0% LLDPE	UC GRSN-7047 LLDPE
DSC					
Tm, °C	159.0	158.3	160.0	160.1	120.9
Crystallinity,%	42.7	46.8	45.6	48.9	48.3
Cryst Temp, °C	109.6	111.6	120.6*	*121.0	104.6
Cryst Rate, mw/min/mg	0.037	0.131	3.094	4.830	None at 125,100
Cryst Time, min	13.3	8.6	2.7	2.6	90, 80°C
GPC					
$\overline{Mw}$	439,900	341,500	350,200	339,500	195,100 **
$\overline{Mn}$	72,200	69,200	72,800	69,200	48,200
Z	1,543,100	1,016,000	982,000	963,500	572,500
$\overline{Mw}/\overline{Mn}$	6.1 →	4.9	4.8	4.9	4.1
(n)	2.4	2.0	2.1	2.0	1.4
Melt Flow, L	0.7	1.9*	2.1	2.2	1.7*
% Haze					
(50 mil C.M.)	46.1	57.5	47.5	42.5	94.0
(50 mil I.M.)	34.9	55.2	35.3	36.8	--
(2 mil C.F.)	8.5	30.5	5.7	6.8	--

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* Additives: Irganox 1010, 0.25% Millad 3905.
** Not corrected for PE.

NOTE: CM - Compression Molded
IM - Injection Molded
CF - Cast Film

Referring to Table I, it can be seen that the addition of peroxide to the base resin (fractional melt flow homopolymer) both narrows the molecular weight distribution and increases the percent haze of injection molded, compression molded and cast film samples (blends I and II). Addition of a nucleating agent (blend III) increases the crystallization temperature from approximately 110°C to 120°C and decreases the haze to that of the "starter" material, PP-A. The subject blend of this invention, blend IV, shows the addition of 1.0% LLDPE. In the absence of a nucleating agent, the LLDPE (column V) is considered "incompatible" with the CR ("controlled rheology") polypropylene; however, in the nucleated CR-polypropylene, (column IV), the melting point (Tm) of the LLDPE occurs at the crystallization temperature (Tc) of the polypropylene. This thermal balance, [(Tm)LLDPE = (Tc)PP = 120°C], and the concurrent crystallization of polyethylene and polypropylene may contribute to low haze and improved physical properties attainable only through the combination of peroxide, nucleation, and addition of LLDPE. As a result, the subject blend may involve solid-liquid separation behavior, co-crystallization of the normally very slow crystal growth LLDPE and the fast growth polypropylene, or amorphous phase compatibility between the two polymers. While accurate results are difficult to obtain with concentrations of LLDPE in polypropylene within the bounds of my invention, results with higher concentration of LLDPE indicate that the annealed differential scanning calorimetry curve will show an upward shift in crystallization temperature (Tc) of the LLDPE from about 105°C to 115°C. This higher crystallization temperature "interferes" with the normal crystallization rate of the nucleated polypropylene. The LLDPE appears to crystallize concurrently with the polypropylene. As previously mentioned, the melting point of the LLDPE is at the crystallization temperature of the polypropylene.

FILM SAMPLES

The general trends in physical properties determined on 4-inch wide, 2 mil thick cast film from blends similar to those in Table I show the following resin-component interactions:

CONTROL RESIN: 4 melt-flow, homopolymer film grade resin.

Interaction :	Results
PP-A + Peroxide (4 melt flow)	- narrow molec. wt. distribution. - very high impact properties. - low tensile yield strength. - high percent haze. - film is too "flexible".
PP-A + Peroxide + LLDPE	- incompatible blend. - very high percent haze. - large property imbalance (longitudinal vs. transverse direction).
PP-A + Peroxide + Nucleation (Millad 3905)	- physical properties similar to a 4 melt-flow reactor product. - no apparent incentive to use this material.
PP-A + Peroxide + Nucleation + LLDPE	- low haze product. - high yield strength. - very high ultimate elongations (10-15% greater than control). - exceptional bi-directional property balance.

Some specific physical properties relative to film (Table II) confirm the general trends reported in Table I on resin-component interactions. Compared with a 4 melt-flow homopolymer made in a reactor (sample I), the 4 melt-flow CR product (sample II) has a lower tensile yield strength, a higher ultimate elongation and a high haze. Adding a nucleating agent (sample III) does not produce a material significantly different from the reactor product; however, the combination of the nucleating agent and LLDPE (blend IV) results in improved modulus, yield strength, elongation and haze.

Film is generally defined in the trade as being 10 mils or less in thickness; above 10 mils and up to about .05 in., the product is known as a sheet. My invention is useful for both biaxially oriented sheet and biaxially oriented film.

Table II

PHYSICAL PROPERTIES 4-in. wide film x 2.2 mil thick

		I PP-B***	II (Control) PP-A + Peroxide	III Control + Nucleation	IV Control + Nucleation + LLDPE
Tensile Modulus x 10^5 PSI	MD*	2.46	2.12	2.14	2.38
	TD**	1.66	2.08	2.28	2.42
Tensile Yield Strength, PSI	MD	3800	3120	3900	4340
	TD	3600	3060	3820	4160
Ultimate Elong, %	MD	534	600	680	675
	TD	807	866	750	946
Haze, %		8.5	30.5	5.7	6.8

* Machine direction.
** Transverse direction.
*** 4-melt flow reactor homopolymer.

Additional data is presented on laboratory-prepared film extrusion cast onto a chill roll. Results in Table III show that the blend of my invention, 88-7U, exhibits an improvement in physical properties compared with a similar melt flow reactor-made homopolymer control resin. The new film, containing the nucleating agent (0.25% Millad 3905) and 1.5% LLDPE, has exceptional ultimate elongation in both the longitudinal direction (MD) and transverse direction (TD). Melt orientation of the blend (achieved by increasing roll speed 33%) results in film with a very high tensile modulus; other properties are similar to those of the control resin.

Table III

Tensile Properties of High-Clarity Film* Extruded From Polypropylene 88-7U

Control	Tensile Modulus x 10^5, psi MD	Tensile Modulus x 10^5, psi TD	Yield Strength, psi MD	Yield Strength, psi TD	Yield Elongation, % MD	Yield Elongation, % TD	Tensile Strength, psi MD	Tensile Strength, psi TD	Ultimate Elongation, % MD	Ultimate Elongation, % TD
PP-B	2.47	1.66	3790	3620	13.2	12.5	4150	4080	534	807
(SD)***	0.18	0.12	104	143	0.69	0.74	349	460	156	117
COV,%+	7.2	7.8	2.7	4.0	5.3	5.9	8.4	11.3	34.7	14.4
88-7U	2.88	1.88	4320	4020	13.2	12.4	4760	4410	763	920
(SD)	0.36	0.14	67.2	94	0.41	0.84	398	518	51	139
COV,%	12.6	7.7	1.6	2.3	3.1	6.8	8.4	11.7	6.7	15.1
88-7U** MD Oriented	5.88	2.28	3910	3830	15.7	13.8	4230	4150	589	798
(SD)	0.34	0.20	49.2	168	0.02	0.01	626	354	56.3	47.8
COV,%	5.9	9.0	1.3	4.3	0.1	0.1	14.8	8.4	9.6	6.0

* Chill-roll cast film (~2.0 mil thick by 3.75 in. wide) tested at 2.0 in./min CRS, 2.0 inch gage length. Film extrusion melt: 467°F, roll temperature 62°F.

** MD orientation achieved by increasing roll speed 33 percent.

*** Standard Deviation.

\+ Coefficient of Variation.

Unlike the chill-roll cast film previously reported, film in Table IV was made by water-quenching the extrudate. Blend 88-7 containing 1.5% LLDPE and 0.25% Millad 3905 has an excellent surface appearance, is approximately 9% less in film width, and has a low (8.8%) haze compared with a similar melt flow reactor-made homopolymer.

Table IV

Characteristics of Water-Quench Film from Nucleated CR/LLDPE

Control Samples*	Haze Sample Thickness	Width	Appearance	% Haze
PP-C*	1.5-2.0	5.625	No orange peel No wrinkles	19.0
PP-D**	1.5-2.2	5.500	Very fine orange peel (acceptable) wrinkles, one poor edge	12.8
88-7 (invention) (1.5 LLDPE 0.25 M-3905)	1.5-2.0	5.094	Excellent film No orange peel Clearer than F-040F	8.8
PP-E +	1.5 (OPP)	-	Excellent production quality, biaxial orientation	0.65

* 4-melt flow homopolymer, not cracked, not film grade.

** 4-melt flow commercial film grade homopolymer.

\+ a 2.5 melt flow reactor film grade homopolymer, commercial biaxial oriented polypropylene film (OPP).

Physical properties on biaxially oriented film are shown in Table V. Compared to conventional homopolymer film, film made from the blend is easier to orient in the longitudinal direction (MD); orientation in the lateral direction (TD) can be done at lower temperatures and higher stretch ratios than commonly used for homopolymer.

INJECTION MOLDED SAMPLES

Tables VI and VII relate the Izod Impact Strength of the subject blend. Results show (Table VI) impact properties of the blend are greater than 1.0 ft-lb/in. notch and annealed samples have an impact strength greater than 12 ft-lb/in. notch with all partial sample breaks. Results in Table VII show the Izod Impact Strength is affected by the molding temperature. The impact strength ranges from 1.17 ft-lb/in.(N) at 450^{O}F to 4.40 ft-lb/in.(N) at 430^{O}F. These properties are the result of molding oreintation, the interaction between the peroxide with the two polymers (PP-LLDPE), and the nucleating agent. This type of behavior is not observed in conventional film-grade polypropylene.

Table V

*BIAXIAL ORIENTATION OF LOW MELT FLOW NUCLEATED CR CONTAINING 1.5 PERCENT LLDPE (1.0 mil Film)

Tensile Modulus x 10^5 PSI		Tensile Strength PSI		Percent Elongation	
MD	TD	MD	TD	MD	TD
3.3 (0.19)	6.1 (0.25)	19,540 (1690)	29,240 (2610)	83 (11.6)	39 (9.7)

* 48 mil Sheet stretched 6:1 in Machine Direction (MD) at 290°F and 8:1 in Transverse Direction (TD) at 330°F to produce a 1.0 mil Film.

Standard Deviation (0.00)

Table VI

Izod Impact Strength vs. Room Temperature Age Time for Blends 88-13 and 88-14**

	Izod Impact (ft-lb/in. notch)	Standard Deviation
88-13 (1.5% LLDPE)		
24 hours	1.28	0.03
48 hours	1.27	0.03
72 hours	1.24	0.02
144 hours	1.24	0.05
144 hours (annealed)*	12.8 (partial break)	0.24
88-14 (0.5% LLDPE)		
24 hours	1.25	0.02
48 hours	1.23	0.02
72 hours	1.19	0.02
144 hours	1.20	0.04
144 hours (annealed)*	12.5 (partial break)	0.29

* Annealed @ 140°C for 2 hours, slow-cooled to room temperature, notched, and tested.

** 88-13 and 88-14 are PP-A which has been "cracked" through the addition of a peroxide as in column IV of Table I, containing 1.5% and 0.5% LLDPE, respectively.

Table VII

Effect of Molding Temperature on the Izod Impact Strength of Low Melt-Flow Nucleated CR containing 1.5% LLDPE

Injection Molding* Cylinder Temperature, °F	430	440	450
Samples Tested/Izod Impact Strength, ft-lb/in(N)	10/4.40	7/1.19 3/3.93	9/1.17
Standard Deviation	0.23	0.06	0.03

* Mold Temperature 140°F

For example, Tensile-Impact data in Table VIII show the desirable effect of the additive combination. Unlike the Izod test, the Tensile Impact test measures energy to rupture by rapid stretching. It is a high speed test in which crack-failure is initiated and propagated in the absence of a notch. Because of material elongation, the test is sensitive to failure mechanisms different from those found in Izod or falling-weight impact testing. The effect of peroxide on the starter material (PP-A) is a property imbalance (composition II). A high percent haze is accompanied by a high impact strength in the flow-direction of the molded die-cut specimen and a drop in impact strength of the transverse-to-flow direction (TFD) sample. The nucleated CR blend (Millad 3905) has similar, or in some cases lower, properties than the control material (see blend III). An improvement in both FD (flow direction) and TFD strength is observed (blend IV) with the addition of both Millad and LLDPE to the CR material. The blend has a low percent haze, uncharacteristic of low-melt flow CR. In blend V, the Millad nucleating agent is omitted. The LLDPE results in a high percent haze and an imbalance in impact properties.

Table VIII

TENSILE IMPACT PROPERTIES OF MODIFIED POLYPROPYLENE*

	I		II		III		IV		V	
	PP-A		PP-A + 100 ppm Lupersol 101		PP-A Nucleated CR (See Additives)		PP-A Nucleated CR + 0.5% LLDPE		PP-A (Not Nucleated) CR + 0.5% LLDPE	
Melt Flow, (L)	0.72		1.9		2.1		1.9		2.1	
	FD	TFD	FD	TFD	FD	TFD	FD	TFD	FD	TFD
Tensile-Impact ft-lb/in^2	79.0	10.3	96.4 (Stress—whiten on failure)	7.4	77.7	9.0	89.7	12.5	108.1	5.4
% Haze Compression Molded Plaque	46.1		54.3		47.5		42.3		51.5	

Additives

500 ppm Irganox 1010
120 ppm Lupersol 101
0.25% Millad 3905

* ASTM D1822, Type-L Bars Die-Cut (Flow Direction/Transverse Flow Direction) from 50-mil Injection-Molded Plaques.

CLAIMS:

1. A polypropylene composition comprising:

(a) a propylene polymer having a melt flow of about 2.0 to about 5.0 g/10 min.(L),

(b) about 0.10 wt % to about 0.25 wt % dibenzylidene sorbitol nucleating agent and

(c) a linear low density ethylene copolymer comprising ethylene copolymerised with olefin monomers having about 4 to about 8 carbon atoms,

characterised in that

said propylene polymer (a) is a propylene homopolymer; said dibenzylidene sorbitol nucleating agent (b) is a bis (alkylbenzylidene) sorbitol wherein the alkyl groups have about 2 to 18 carbon atoms; and said linear low density ethylene copolymer (c) comprises ethylene copolymerized with about 0.5 to about 7% of said olefin monomers, has a melting point of about 120°C and is present in an amount of about 0.25 wt % to about 2.0 wt %.

2. The polypropylene composition of claim 1 wherein the propylene homopolymer is formed by cracking a lower melt flow polypropylene using a peroxide agent selected from the group consisting of dialkyl peroxides in an amount of about 50ppm to about 300ppm.

3. The polypropylene composition of claim 2 wherein the cracking takes place in an extruder.

4. The polypropylene composition of any of claims 1 to 3 wherein the propylene homopolymer has a molecular weight distribution of about 2 to about 4 and a crystallisation temperature of about 120°C.

5. Biaxially oriented sheet made from the polypropylene composition of any of claims 1 to 4.

6. Biaxially oriented film made from the polypropylene composition of any of claims 1 to 4.